POLYMERIZATION REACTIONS

• Understand the differences between step-growth and chain-growth polymerization reactions.
• Predict the products of polycondensation and polyaddition reactions.
• Explain how reactant ratios and monomer purity may affect the degree of polymerization.
• Understand the initiation, propagation, and termination processes in free-radical, ionic, coordination (Ziegler-Natta), and ring-opening polymerizations.
• Explain how the nature of the reaction catalyst influences polymer structure (stereoregularity and tacticity).

STEP-GROWTH POLYMERIZATION

• Formerly: Condensation polymerization (Carothers, 1931)
• Monomers are difunctional — each has two reactive functional groups
• Chain growth occurs through coupling (condensation, addition) reactions
• [Monomer] decreases rapidly before any high-MW polymer is formed
• Rate of polymerization is highest at outset, decreases as chain ends are consumed ⇒ long reaction times
**Schematic:**

\[ nA + nB \rightarrow (A-B)^n \]

**Addition:** \[ nA + nB \rightarrow (A-B)^n \]

**Condensation:** \[ nA + nB \rightarrow (A-B)^n + Y \]

The number average **degree of polymerization** \((X_n)\) is

\[ DP = X_n = \frac{N_0}{N} = \frac{\text{Number of molecules at start}}{\text{Number of molecules at end}} \]

The ratio \([A]:[B]\) strongly influences chain length

<table>
<thead>
<tr>
<th>(N_0/N)</th>
<th>(X_n)</th>
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</thead>
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<tr>
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<td>12/2</td>
<td>6</td>
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<td>12/1</td>
<td>12</td>
</tr>
</tbody>
</table>
Degree of Polymerization

Representative Step-Growth Reactions

Condensation Reactions

Polyester (Polyethylene terephthalate/PET)

\[ \text{HO-}-(\text{CH}_2)_2\text{OH} + \text{HOOC-}-(\text{CH}_2)_2\text{COOH} \rightarrow \text{H}_2\text{O} \]

Polyamide (Nylon-6,6)

\[ \text{H}_2\text{N-}-(\text{CH}_2)_2\text{NH}_2 + \text{HOOC-}-(\text{CH}_2)_2\text{COOH} \rightarrow \text{H}_2\text{O} \]

Addition Reactions

Polyurethane

\[ \text{HO-}-(\text{CH}_2)_2\text{OH} + \text{OCN-}-(\text{CH}_2)_2\text{NCO} \rightarrow \text{DABCO} \]

See also Table 3.2, pp 25-26
Predicting Molar Mass in Step-Growth Pzns

The **extent of reaction** \((p)\) is

\[
p = \frac{\text{Number of functional groups reacted}}{\text{Initial number of functional groups}}
\]

Since the total number of molecules \((N)\) decreases by 1 for each condensation step,

\[
p = \frac{N_0 - N}{N_0} \quad \text{or} \quad \frac{N_0}{N} = \frac{1}{1-p}
\]

\[X_n = \frac{1}{1-p}\] Carothers equation

---

Carothers Equation

![Graph of Carothers Equation](image)
Step-Growth Reactions: MW Distribution

\[ X_n = \frac{N_0}{N} = \frac{1}{1-p} \]

The corresponding weight-average degree of polymerization is

\[ X_w = \frac{1+p}{1-p} \]

The molecular weight distribution (polydispersity) is therefore

\[ \frac{X_w}{X_n} = 1 + p \]

\[ \Rightarrow as \ p \to 1, \ MWD \to 2 \] for any linear step-growth pzn

Molecular Weight Control

\[ nA + nB \to (A-B)_n \]

• Lowering the temperature before the reaction is complete can reduce product MW.
  Result: a thermally unstable product.

• Alternative: use a non-stoichiometric reactant ratio \([A] < [B]\). The less abundant reactant is consumed completely.
  In terms of functional groups \(N_A < N_B\), the reactant ratio is

\[ r = \frac{N_A}{N_B} < 0 \]

Substituting gives the general Carothers equation:

\[ X_n = \frac{1 + r}{1 + r - 2rp} \]
Molecular Weight Control (cont.)

\[ X_n = \frac{1 + r}{1 + r - 2rp} \]

<table>
<thead>
<tr>
<th>( r )</th>
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<th>( p = 0.950 )</th>
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<tr>
<td>0.990</td>
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<td>66.8</td>
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<td>0.950</td>
<td>8.1</td>
<td>13.4</td>
<td>28.3</td>
<td>37.6</td>
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<tr>
<td>0.900</td>
<td>6.8</td>
<td>10.0</td>
<td>16.1</td>
<td>18.7</td>
</tr>
</tbody>
</table>

Molecular Weight Control (cont.)

Producing high-MW step-growth polymers requires

- High conversions \((p > 0.98)\)
- Stoichiometric ratios of functional groups
- High-purity monomers
- No side reactions
CHAIN-GROWTH POLYMERIZATION

- Formerly: Addition polymerization (Carothers, 1931)
- Polymerization requires an initiator, a substance that starts the reaction
- Chain growth occurs by addition of monomer to a relatively small number of initiation sites (free radicals, anions, cations, transition metal complexes)
- Reaction mixture contains monomer, high polymer, and a low concentration of growing chains
- [Monomer] decreases steadily as polymer is formed

Schematic:

\[ nM \rightarrow M_n^- \]

Initiation: \[ I + M \rightarrow I-M^* \]
Propagation: \[ I-M^* + nM \rightarrow I-M_n-M^* \]
Termination: Reactions depend on M and M*

\[ \text{DP} = \frac{X_n}{M} = \frac{\text{Moles of monomer consumed}}{\text{Moles of chains produced}} \]

The ratio [initiator]:[monomer] strongly influences chain length


**Degree of Polymerization**

![Graph showing the relationship between reaction step number and degree of polymerization.](image)

- **Mol$_{cons}$**
- **$X_n$**

<table>
<thead>
<tr>
<th>Reaction Step Number</th>
<th>Degree of Polymerization</th>
</tr>
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<tbody>
<tr>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
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<tr>
<td>2</td>
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<td>11</td>
<td>11</td>
</tr>
<tr>
<td>12</td>
<td>12</td>
</tr>
</tbody>
</table>
Representative Chain-Growth Reactions

**Free-Radical Vinyl Pzns**

Poly(methyl methacrylate)

\[
\text{H}_2\text{C} = \underset{\text{CH}_2}{\text{COOCH}_3} \xrightarrow{\text{K}_{\text{R,S}} \text{H}_2\text{O}} \underset{\text{CH}_2}{\text{-- COOCH}_3}\n\]

**Carbocationic/Anionic Pzns**

Butyl Rubber (IIR)

\[
\text{H}_2\text{C} = \underset{\text{CH}_3}{\text{CH}_2} + \underset{\text{CH}_3}{\text{CH}_2} \xrightarrow{\text{AlCl}_3} \underset{\text{CH}_3}{\text{CH}_2} \underset{\text{CH}_2}{\text{-- COOCH}_3} \underset{\text{CH}_3}{\text{CH}_2} \]

**Coordination Pzns**

Polypropylene

\[
\text{H}_2\text{C} = \underset{\text{CH}_3}{\text{CH}_2} \xrightarrow{\text{TiCl}_3/\text{AlCl}_3} \underset{\text{CH}_3}{\text{CH}_2} \underset{\text{CH}_3}{\text{CH}_2} \underset{\text{CH}_3}{\text{CH}_2}\n\]

See also Table 3.2, pp 25-26

Reactant Compatibilities

<table>
<thead>
<tr>
<th>Monomer</th>
<th>Mechanism*</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Radical</td>
</tr>
<tr>
<td>Ethylene</td>
<td>+</td>
</tr>
<tr>
<td>α-Olefins (≥ C3)</td>
<td>-</td>
</tr>
<tr>
<td>1,1-Dialkylalkenes</td>
<td>-</td>
</tr>
<tr>
<td>1,3-Dienes</td>
<td>+</td>
</tr>
<tr>
<td>Styrene, α-Me styrene</td>
<td>+</td>
</tr>
<tr>
<td>Vinyl chloride</td>
<td>+</td>
</tr>
<tr>
<td>Tetrafluoroethylene</td>
<td>+</td>
</tr>
<tr>
<td>Acrylate/methacrylate esters</td>
<td>+</td>
</tr>
<tr>
<td>Acrylonitrile, methacrylonitrile</td>
<td>+</td>
</tr>
<tr>
<td>Vinyl ethers</td>
<td>-</td>
</tr>
<tr>
<td>Vinyl esters</td>
<td>+</td>
</tr>
</tbody>
</table>

*Plus (+) sign = high polymer; minus (−) sign = no reaction or oligomer.

See also Table 5.1, p 124

Vinyl Free Radical Polymerization

- Alkene, 1,3-diene monomers
  - Haloethylenes: \( \text{H}_2\text{C} = \text{CHCl} \)
  - Styrene: \( \text{CH} = \text{CHCH}_2 \)
  - Acrylic, methacrylic acid derivatives: \( \text{H}_2\text{C} = \text{C} = \text{CH}_2 \text{OCH}_3 \)

- Free radical initiators
  - Benzoyl peroxide: \( \text{C}_6\text{H}_5\text{COO}^- \rightarrow 2 \text{C}_6\text{H}_5\text{COO}^- \)
  - Azobisisobutyronitrile (AIBN): \( \text{NC} - \text{C} - \text{C} = \text{N}_2 \rightarrow 2 \text{NC} - \text{C} = \text{C} - \text{N}_2 \)
  - K persulfate (peroxydisulfate): \( (\text{O}_3\text{SO} - \text{OSO}_3)^2^- \rightarrow 2(\text{O}_3\text{SO}^-)^2^- \)

- Thermal, redox, or photochemical initiation

\[
\begin{align*}
\text{Initiation} & \\
\text{(Peroxide)} & \xrightarrow{\Delta} 2 \text{C}_6\text{H}_5\text{COO}^- = \text{I}^- \\
\text{I}^- + \text{H}_2\text{C} = \text{CH} & \rightarrow \text{I}^- \text{CH}_2\text{CH} & \text{Propagation} \\
\text{I}^- \text{CH}_2\text{CH} & \xrightarrow{\text{I}^-} \text{I}^- \text{CH}_2\text{CH} & \rightarrow \\
\end{align*}
\]
Molecular Weight Control

- Most monomer is (or should be) consumed by polymer chain growth, not initiation.
- **Termination** involves reactions that stop polymerization.
- **Chain transfer** to monomer, solvent, or initiator kills the polymer chain but continues the kinetic chain (new chains can be initiated):

  \[ \text{M}_i^+ + X \rightarrow \text{M}_i + X^- \]

- Chain length is proportional to \([M]\) and \(1/\sqrt{[I]}\):

  \[ X_n = K \frac{[M]}{[I]^{1/2}} \]

- To maximize DP, increase \([M]:[I]\) in the reaction mixture or increase \(K\) by the choice of monomer.
Molecular Weight Control (cont.)

If chain transfer processes to both monomer (M) and solvent (S) are important:

\[
\frac{1}{X_n} = \frac{1}{X_{n0}} + C_M + C_S \frac{[S]}{[M]}
\]

Mayo (Mayo-Walling) eqn

where \(X_{n0}\) is the DP you get with no chain transfer.

If transfer to monomer is not important, then

\[
\frac{1}{X_n} = \frac{1}{X_{n0}} + C_S \frac{[S]}{[M]}
\]

Simplified Mayo eqn

The reciprocal of DP should be a linear function of the ratio of [S] to [M]. The slope would be a function of the rate of chain transfer to solvent.

Styrene Pzn: Chain Transfer to Solvent

Styrene Pzn: Chain Transfer to Solvent

\[ M_1 \cdot + X-H \rightarrow M_1H + X \cdot \]

Function slopes show relative ease of radical \((X \cdot)\) formation:

\[
\text{C} \cdot \text{CH}_3 > \text{C} \cdot \text{CH}_3 \text{H} > \text{C} \cdot \text{H} \text{CH}_3 > \text{C} \cdot \text{H} > \text{C} \cdot
\]

Carbocationic Chain-Growth Pzn

- **Alkene, 1,3-diene monomers**
  - Isobutylene (2-methylpropene): \( \text{H}_2\text{C}==\text{C}==\text{CH}_3 \)
  - Isoprene (2-methyl-1,3-butadiene): \( \text{H}_2\text{C}==\text{C}==\text{CH}_2 \text{CH}_3 \)
  - β-Pinene:

- **Lewis acid catalysts**
  - \( \text{AlCl}_3 \)
  - \( \text{BF}_3 \)
  - \( (\text{CH}_3\text{CH}_2)_2\text{AlCl} \)

- **Brønsted acid or carbocation-donor co-catalysts**
  - HCl or \( \text{H}_2\text{O} \):
    
  \[ \text{BF}_3 + \text{H}_2\text{O} \rightleftharpoons \text{F}_3\text{B-OH}_2 \]
  - RCl:
    
  \[ \text{AlCl}_3 + (\text{CH}_3)_3\text{CCl} \rightleftharpoons (\text{CH}_3)_2\text{C}^+\text{AlCl}_4^- \]
**Initiation**

\[
F_3B\cdot OH_2 \rightleftharpoons F_3B\cdot OH^- + H^+
\]

\[
F_3B\cdot OH^- + H^+ + H_2C=CH_2 \rightarrow H_2C-CH-CH_2^- F_3B\cdot OH^-
\]

**Propagation**

**Termination**

**Chain Transfer**

**Quenching**
Molecular Weight Control

\[ \frac{1}{X_n} = \frac{C_t}{[M]} + C_M \]

Simplified Mayo equation

- Reactions are extremely rapid \( \Rightarrow \) controlling heat transfer is important.
- Chain transfer to monomer is often significant.
- DP is independent of initiator concentration.
- For a typical exothermic polymerization, the reaction rate increases as the temperature is reduced.
- Net outcome:
  \[ \text{DP increases at lower temperature} \]

Anionic Chain-Growth Polymerization

- **Alkene, 1,3-diene monomers**
  - 1,3-butadiene: \( \text{H}_2\text{C} \equiv \text{CH} \equiv \text{CH} \equiv \text{CH}_2 \)
  - Styrene: \( \text{CH} \equiv \text{CH}_2 \text{C} \equiv \text{C} \equiv \text{O} \)
  - Methyl methacrylate: \( \text{H}_2\text{C} \equiv \text{C} \equiv \text{C} \equiv \text{OCH}_3 \)
  - Vinyl pyridine: \( \text{CH} \equiv \text{CH}_2 \)

- **Catalysts: Lewis bases, organometallics**
  - \( \text{NH}_2^- \)
  - \( \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Li} \) (\( n \)-butyllithium)
  - \( \text{[\text{C}_6\text{H}_6]}^-\text{Na}^+ \)
**Initiation**

\[ \text{C}_4\text{H}_9\text{Li}^- + \text{H}_2\text{C}==\text{H} \rightarrow \text{C}_4\text{H}_9\text{C}_2\text{Li}^- \]

**Propagation**

\[ \text{C}_4\text{H}_9\text{C}_2\text{Li}^- + \text{H}_2\text{C}==\text{H} \rightarrow \text{C}_4\text{H}_9\text{C}_2\text{C}_2\text{Li}^- \]

**Molecular Weight Control**

- Anionic polymerizations lack inherent termination processes (ion-pair rearrangements, anion-metal cation reactions).
- Monomer molecules only react with the anionic end groups on the propagating polymer chains.
- Polymer chains continue to grow as long as additional monomer is added. These chains are

  **Living Polymers**
Molecular Weight Control (cont)

\[ DP = X_n = \frac{p}{[I]_0} \]

where \( p \) is the fraction of monomer converted.

At complete conversion, \( DP \) is the monomer:initiator ratio at the outset of reaction:

\[ DP = X_n = \frac{[M]_0}{[I]_0} \]

The MWD (polydispersity) is therefore:

\[ \frac{X_w}{X_n} = 1 + \frac{1}{X_n} \]

The MWD of a living anionic polymer will be extremely narrow, tending toward a value of 1 as \( X_n \) increases.

Anionic Pzn as a Route to Block Copolymers

- Living polymerization yields polymer chains with reactive end groups:
  \[ R\text{-}SS\text{-}S\text{-}Li^+ \]

- These living chains can react with a second monomer to extend the chain and create a final product with unique chemical and physical properties:
  \[ R\text{-}SS\text{-}S\text{-}Li^+ + nB \rightarrow R\text{-}SSSS\text{-}BBB\text{-}B^\prime\text{-}Li^+ \]

- Block copolymers comprise two or more homopolymer subunits. These are referred to as \emph{n-block} copolymers.

Commercial block copolymers include SIS (styrene-isoprene-styrene) and SBS (styrene-butadiene-styrene) triblocks.
Controlling Stereochemistry

- Natural polymers have a high level of structural regularity:

\[
\begin{align*}
\text{cis-1,4-Polyisoprene (NR)}
\end{align*}
\]

- Synthetic polymers often contain many structures:

\[
\begin{align*}
\text{1,2-addition} & \quad \text{3,4-addition} & \quad \text{cis-1,4-addition} & \quad \text{trans-1,4-addition}
\end{align*}
\]

**STEREOCHEMISTRY**
Properties that relate to a molecule’s 3-dimensional structure.

Controlling Stereochemistry (cont.)

<table>
<thead>
<tr>
<th>Conditions</th>
<th>IR Structure, mol fraction</th>
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<tbody>
<tr>
<td></td>
<td>cis-1,4</td>
</tr>
<tr>
<td>Free-radical, ~20°C</td>
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</tr>
<tr>
<td>Free-radical, 100°C</td>
<td>0.23</td>
</tr>
<tr>
<td>Anionic, RLi, 30°C</td>
<td>0.94</td>
</tr>
</tbody>
</table>

- Polymer structures depend on
  - Monomer structure and conformation (cisoid vs. transoid)
  - Nature of active unit structure (free radical vs. anion)
  - Stability of active unit structure (cis-trans isomerization in 1,4-addition)
Controlling Stereochemistry (cont.)

Free-radical

1,4-trans addition

Anionic

1,4-cis addition

Ziegler-Natta Catalysis:
Coordination Chain-Growth Polymerization

- Alkene, cycloalkene, 1,3-diene monomers
  - Propylene (Propene): \( \text{H}_2\text{C}═\text{CH}─\text{CH}_3 \)
  - 1,3-Butadiene: \( \text{H}_2\text{C}═\text{CH}═\text{CH}_2 \)
  - 5-Ethylidene-2-norbornene: \( \text{C}═\text{CH}─\text{CH}═\text{CH}_3 \)

- Group 4B-8B transition metal catalysts
  - TiCl$_4$
  - VCl$_4$
  - Ti, Zr metallocenes

- Group 1A-3A metal co-catalysts/activators
  - \((\text{CH}_3\text{CH}_2)_2\text{Al}\) (with TiCl$_4$)
  - \([\text{Al}(\text{CH}_3)\text{O}]_n\) (with titanocene dichloride)
Ziegler-Natta Catalysts

- Active catalyst produced by reaction of transition metal component with Group 1A-3A co-catalyst:
  \[ \text{TiCl}_4 + (\text{C}_2\text{H}_5)_3\text{Al} \rightarrow \text{Cl}_3\text{Ti-C}_2\text{H}_5 + (\text{C}_2\text{H}_5)_2\text{AlCl} \]

- The concentration of active catalyst \([C^*_p]\) is \((0.01-10)n\%\) of [transition metal component].

- Termination reactions are relatively unimportant.
  - DP tends to be high
  - Reactions must be quenched by active H sources (H₂):
  \[ \text{Cl}_3\text{Ti-M}_n\text{C}_2\text{H}_5 + [\text{H}] \rightarrow \text{Cl}_3\text{Ti-H} + \text{H-M}_n\text{C}_2\text{H}_5 \]

Kinetics of Coordination Polymerization (cont.)

Stereochemistry of Polymerization

- The stereochemistry of polymer chain propagation controls the relative stereochemistry (tacticity) of the polymer.
- In ionic polymerizations, high stereoregularity can be achieved if there is strong coordination of the counter-ion with the terminal unit on the growing chain. (Promoted by low reaction T, polar substituent groups)
- Stereoregularity influences chain-chain interactions, chain stiffness, crystallizability.

**TACTICITY**
The relative stereochemistry of adjacent chiral centers within a macromolecule

**ATACTIC**
*random* configurations
**ISOTACTIC**

*identical configurations*

**SYNDIOTACTIC**

*alternating configurations*
### Stereoselective Polymerizations

<table>
<thead>
<tr>
<th>Monomer</th>
<th>Conditions</th>
<th>Structure</th>
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<tbody>
<tr>
<td>IsoC₄ vinyl ether</td>
<td>Et₂O-BF₃ in propane, −80 to −60°C</td>
<td>isotactic</td>
</tr>
<tr>
<td>Me methacrylate</td>
<td>n-C₆H₁₃Li in toluene, −78 to 0°C</td>
<td>isotactic</td>
</tr>
<tr>
<td></td>
<td>n-C₆H₁₃Li in THF, −78°C</td>
<td>syndiotactic</td>
</tr>
<tr>
<td>Propylene</td>
<td>TiCl₄-Et₂Al in heptane, 50°C</td>
<td>isotactic</td>
</tr>
<tr>
<td></td>
<td>VCl₄-Et₂Al + PhOCH₃ in toluene, −78°C</td>
<td>syndiotactic</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Property</th>
<th>Atactic Polypropylene</th>
<th>Isotactic Polypropylene</th>
<th>Syndiotactic Polypropylene</th>
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</thead>
<tbody>
<tr>
<td>Melting point, °C</td>
<td>---</td>
<td>160-171</td>
<td>130-160</td>
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<tr>
<td>Crystallinity, %</td>
<td>0</td>
<td>55-65</td>
<td>50-75</td>
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</table>


### Comparing Step-Growth & Chain–Growth Pzn

<table>
<thead>
<tr>
<th></th>
<th>Step-Growth</th>
<th>Chain-Growth</th>
</tr>
</thead>
<tbody>
<tr>
<td>Monomer addition</td>
<td>Any two species can combine (monomer or polymer)</td>
<td>Rapid addition to small number of active centers</td>
</tr>
<tr>
<td>Reaction rate</td>
<td>Much slower than chain growth</td>
<td>Rapid and constant</td>
</tr>
<tr>
<td>MW growth</td>
<td>Increases continuously as monomers react</td>
<td>High MW present even at low conversion</td>
</tr>
<tr>
<td>Process type</td>
<td>Batch</td>
<td>Continuous, semi-batch</td>
</tr>
<tr>
<td>Examples</td>
<td>Nylon, PETE</td>
<td>BR, IR, SBR, IIR, EPM, EPDM</td>
</tr>
</tbody>
</table>

Adapted from ExxonMobil Chemical "Polymer Technology Course" 2009.
RING-OPENING POLYMERIZATION

• Chain-growth reactions. Proceed by relieving
  – Strain in small-ring monomers
  – Steric crowding in large-ring monomers

• Reactions are catalyzed by
  – Free radicals
  – Anions
  – Cations
  – Transition metal-carbene complexes

\[ \text{Example:} \quad \begin{array}{c}
\text{Ru}=\text{C} \\
\text{Cl} \\
\text{(C}_6\text{H}_{11})_3\text{P}
\end{array} \]

RING-OPENING PZN (cont.)

• Polymerizations follow two general pathways:
  – Ring opening of cyclic monomers: ethers (epoxides), esters (lactones), amides (lactams), etc.
  – Ring-opening metathesis polymerization (ROMP) of olefins: cycloalkenes, bicycloalkenes

\[ n \left( \text{CH}_2 \right)_x \rightarrow \left( \text{CH}_2 \right)_x \quad Y = O, \text{COO, CONH} \]

METATHESIS
The exchange or transposition of bonds between two reactants
Representative Ring-Opening Pzs

Ring-Opening Pzn of Epoxides
Polyethylene glycol (PEG) from ethylene oxide
\[ n \text{H}_2\text{C}=\text{O} \xrightarrow{\text{HOCH}_2\text{CH}_2\text{OH} / \text{KOH}} \text{HOCH}_2\text{CH}_2\left(\text{OCH}_2\text{CH}_2\text{O}\right)_{n-1}\text{CH}_2\text{CH}_2\text{OH} \]

Ring-Opening Pzn of Lactams
Nylon-6 from \( \varepsilon \)-caprolactam
\[ n \text{H}_2\text{C} \xrightarrow{\text{H}_2\text{C} \text{NH}} \left\{ \text{O} \left[ \text{C} \text{CH}_2\text{CH}_2\text{CH}_2\text{NH} \right] \right\}_n \]

ROMP of Bicycloalkenes
Polynorbornene Rubber (PNR)
\[ n \text{C}_2\text{H}_2 \xrightarrow{\text{RuCl}_3 / \text{HCl} / \text{C}_4\text{H}_9\text{OH}} \left\{ \text{C} \text{H} \right\}_n \xrightarrow{\text{C}_2\text{H}_2 / \text{OH}} \left\{ \text{C} \text{H} \right\}_n \]

COPOLYMERIZATION

- Simultaneous polymerization of two or more monomers yields copolymer with unique properties unlike those of homopolymers from each monomer.
- Copolymers with irregular (random) monomer sequences can have rubber-like properties because of reduced crystallinity.
- Appropriate reaction conditions can provide a range of tailored structures:
  - Random (statistical) - ABABABABABABABABAB-
  - Alternating - ABABABABABABABABAB-
  - Block - AAAAABBBAAAAABBBABBB-
  - Graft - AAAAAAAAAAAAAAAAAAAA-
    BBBB    BBBB
Composition Control

- Monomers differ in their ability to copolymerize.

- The relative rates of monomer reaction are a function of the monomer concentrations ([M_1],[M_2]) and the monomer reactivity ratios (r_n):

\[
\begin{align*}
    r_1 &= \frac{k_{11}}{k_{12}} \\
    r_2 &= \frac{k_{22}}{k_{21}}
\end{align*}
\]

where \( k_{ij} \) is the rate constant for the reaction of monomer i with monomer j.

- Reactivity ratios determine copolymer composition and structure.

Free Radical Pzn: Reactant Ratios

<table>
<thead>
<tr>
<th>Monomer 1</th>
<th>( r_1 )</th>
<th>Monomer 2</th>
<th>( r_2 )</th>
<th>T, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethylene</td>
<td>0</td>
<td>Acrylonitrile</td>
<td>7</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td>0.79</td>
<td>Vinyl acetate</td>
<td>1.4</td>
<td>130</td>
</tr>
<tr>
<td></td>
<td>0.58</td>
<td>1,3-Butadiene</td>
<td>1.4</td>
<td>50</td>
</tr>
<tr>
<td>Styrene</td>
<td>0.29</td>
<td>Acrylonitrile</td>
<td>0.020</td>
<td>60</td>
</tr>
<tr>
<td></td>
<td>55</td>
<td>Vinyl acetate</td>
<td>0.01</td>
<td>60</td>
</tr>
<tr>
<td></td>
<td>0.78</td>
<td>1,3-Butadiene</td>
<td>1.4</td>
<td>5</td>
</tr>
<tr>
<td>Me acrylate</td>
<td>0.84</td>
<td>Acrylonitrile</td>
<td>1.5</td>
<td>50</td>
</tr>
<tr>
<td></td>
<td>6.4</td>
<td>Vinyl acetate</td>
<td>0.03</td>
<td>60</td>
</tr>
</tbody>
</table>

Composition Control (cont.)

Limiting (or idealized) reactivity ratios:

- \( r_1 = r_2 = 0 \) Neither chains end adds its own monomer. Results: 1. a perfectly alternating copolymer and 2. an azeotropic copolymer composition (the ratio of monomers in the feed = the ratio of monomer units in the copolymer).

- \( r_1 = r_2 = \infty \) Each chain adds only its own monomer. Result: a mixture of homopolymers.

- \( r_1 r_2 = 1 \) or \( r_1 = r_2 = 1 \) All chain ends add either monomer with equal probability in an ideal copolymerization. Result: a random copolymer.

Composition Control (cont.)

- In most cases \( r_i \) is not exactly 0, 1, or \( \infty \); polymers tend toward a particular composition and type of structure.

- Comonomer sequences can be inferred from \( r_1 r_2 \) values:
  - \( r_1 r_2 < 1 \) Tendency toward alternating structure
  - \( r_1 r_2 > 1 \) Tendency toward block structure
  - \( r_1 r_2 >> 1 \) Tendency toward homopolymer structure

- When \( r_1 \gg 1 \gg r_2 \) there is copolymer composition drift.
  - At low conversions, the copolymer is enriched in the more reactive monomer.
  - At high conversions, the copolymer is enriched in the less reactive monomer that remains.

- Composition drift can be reduced by delayed or (semi-batch) continuous addition of the more reactive monomer.
Composition Control (cont.)

In terms of the mole fraction \( f \) of each monomer in the co-monomer mixture,

\[
f_1 = \frac{[M_1]}{[M_1] + [M_2]} \quad f_2 = 1 - f_1 = \frac{[M_2]}{[M_1] + [M_2]}
\]

the copolymer equation, expressed as the mole fraction \( F \) of each monomer unit in the copolymer chain, is:

\[
F_1 = \frac{r_1 f_1^2 + f_1 f_2}{r_1 f_1^2 + 2 f_1 f_2 + r_2 f_2^2}
\]

\[
F_2 = 1 - F_1
\]

These equations can be used to calculate the relationship of reactant feed composition to instantaneous polymer composition for various reactant ratios.

Copolymer Composition: Impact of \( r_1 r_2 \)

![Copolymer Composition Graph](image)

Pzn Reactions 4-28
Exercise

The graph shows the feed and product compositions for the free-radical reaction of styrene (monomer 1) and acrylonitrile (monomer 2).

What feed composition do you need to get a copolymer that is 50% styrene?

a) About 55% styrene
b) About 55% acrylonitrile
c) About 25% styrene

What kind of copolymer will you get?

a) One that tends to have an alternating structure.
b) One that is enriched in styrene.
c) One that tends to be a mixture of copolymers.